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Report No. IITRI-C6014-18
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS
(PAINTS WITH LOW SOLAR ABSORPTANCE/
EMITTANCE RATIOS)

George C. Marshall Space Flight Center
National Aeronautics and Space Administration
Huntsville, Alabama

IIT RESEARCH INSTITUTE

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DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS
(PAINTS WITH LOW SOLAR ABSORPTANCE/EMITTANCE RATIOS)

Contract No. NAS8-5379
IITRI Project C6014

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FOREWORD

This is Report No. IITRI-C6014-18 (Triannual Report) of

IITRI Project C6014, Contract No. NAS8-5379, entitled "Investi-

gation of Environmental Effects on Coatings for Thermal Control

of Large Space Vehicles." The report covers the period from

June 20 through October 20, 1964. Previous Triannual Reports

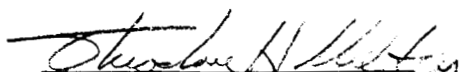were issued on October 25, 1963, March 5, 1964, and July 20,

1964.

Major contributors to the program included Gene A. Zerlaut,

Project Leader; John E. Gilligan, general consultation; Yoshiro

Harada, inorganic coatings; Warren Jamison and William E.

Courtney, space chamber studies; Lawrence U. Berman, silicone

synthesis and photolysis studies; Richard C. Reichel, micro-

porous structures; and Douglas G. Vance, silicone paint

preparation and reflectance measurements. The following people

contributed to this report; L. U. Berman, J. E. Gilligan, Y.

Harada, R. C. Reichel and G. A. Zerlaut.

Data are recorded in IITRI Logbooks C13423, C13736,
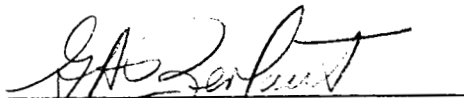
C13802, and C14176.

Respectfully submitted,

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ABSTRACT

DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS
(PAINTS WITH LOW SOLAR ABSORPTANCE/
EMITTANCE RATIOS)

This report describes studies aimed at the development
of stable thermal-control coatings with the lowest possible
ratio of solar absorptance to infrared emittance. Included
are discussions of microporous coating investigations, inorganic
pigment and binder studies, and methyl silicone synthesis and
silicone photolysis experiments.

Recent experiments on the foaming of LTV-602 and other
silicone materials are discussed in detail. The effects of
space simulation (e.g., ultraviolet irradiation in vacuum) on
foamed LTV-602 were found to be very severe. The probable
reasons are thought to involve both the random, deep scattering
of ultraviolet and to contamination from residual Porofor N
blowing agent. Future foaming experiments should involve the
development of polymerization reactions which simultaneously
evolve a gaseous product.

The inorganic studies have indicated that zinc titanate-
potassium silicate paints are relatively stable to ultraviolet
radiation in vacuum. A solar absorptance of 0.12 has been
achieved with a zinc titanate paint. Severe damage was exhibited
by barium sulfate, zirconia, dysprosium oxide, lithium aluminum
silicate (Lithafrax) and "zirconium-spinel" when irradiated as
powders for only 230 ESH (listed in decreasing degree of damage).
In general, both heat treatment and chemical treatment such as
acid washing have been found to improve resistance to ultraviolet
irradiation in vacuum. Exceptions were magnesium aluminate-
spinel and zinc titanate coatings which exhibited poorer resist-
ance after heat treatment.

The discussion of the pertinent literature on silicone
photolysis -- from the viewpoint of gamma-irradiation due to
the paucity of work reported on ultraviolet effects -- was
continued from the previous Triannual Report. The apparatus
which has been constructed for photolysis experiments is described.
Experiments which resulted in preparation of a highly purified
polydimethylsiloxane are discussed in detail.

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DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS
(PAINTS WITH LOW SOLAR ABSORPTANCE/EMITTANCE RATIOS)

I. INTRODUCTION

The general requirement under this contract is for thermal control surfaces with very low, but stable, solar absorptance (α_s) to infrared emittance (ϵ) ratios. Thus, we have attempted to minimize α_s and the effects (on α_s) of simulated solar radiation in vacuum. Due to the generally high emittance of reasonably thick films of dielectric materials, we have not actively pursued studies on the emittance of candidate coatings. Furthermore, the total emittance of nonmetallic coatings is essentially unaffected by ultraviolet irradiation.

Because of the exceptional stability of zinc oxide pigmented coatings (Report No. IITRI-C207-25, August 27, 1964, and Report No. IITRI-C207-27, January 9, 1964), early investigations were aimed principally at (1) techniques to increase the ultraviolet reflectance of zinc oxide paints at little or no expense to either their infrared reflectance or their stability and (2) the development of microbubble structures in paint vehicles.

The use of mixtures containing zinc oxide and a secondary ultraviolet-reflecting pigment has been generally unsuccessful in improving the ultraviolet reflectance and thus the solar

absorptance of corresponding paints. However, the use of
overlayers of ultraviolet-reflecting coatings appears to hold
some promise for decreasing the solar absorptance of zinc
oxide paints. The principal problem with this concept (e.g.,
with topcoats such as zircon, zirconia, or Lithafrax paints)
is the competition between coatings thick enough to provide re-
flectance reinforcement in the ultraviolet and coatings thin
enough not to detract significantly from the ultraviolet
stability of the zinc oxide-pigmented system.

The investigations of microbubble coatings have indicated
a potential for this type of scattering system. However, the
principal limitation in using microporous coatings (unpigmented)
is the stability that can ultimately be achieved with polymeric
films used as the pore-matrix. The problems associated with
the development of stable microporous coatings are discussed
in some detail in the following section.

These foregoing considerations have played a large part in
formulating the plans for the work that is currently being
performed. For example, more emphasis is being given to the
search for a "dielectric" pigment that is as stable as zinc
oxide. Furthermore, a comprehensive study of the mechanisms
associated with ultraviolet photolysis of methyl and methyl/
phenyl silicone polymers is under way. Indeed, our recent ob-
servations involving the significance of residual aromatic

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(toluene) solvent contamination (Report No. IITRI-C6014-13, Triannual, July 20, 1964) have underscored both the urgency for a careful examination of the ultraviolet photolysis of silicone polymers as well as the necessity for reexamination of the potential of microbubble coatings.

II. DEVELOPMENT OF MICROPOROUS STRUCTURE IN PAINT VEHICLES

A. Introduction

In theory, a coating composed of appropriately sized voids, uniformly dispersed in a matrix, should scatter light not unlike a pigmented film. That is, each void (or microbubble) behaves as a scattering center in which the scattering power depends upon refractive index ratios of less than unity (compared with ratios greater than unity for classical pigmented systems). Therefore, the micropores in a foamed coating are in theory the ultimately stable, wholly transparent, non absorbing pigment. A white paint appears white because the numerous scattering events that take place within the white coating effectively scatter the incident white radiation back out of the coating without selective absorption.

A highly reflective microbubble coating must contain voids whose average diameter is roughly 0.5μ. Such voids must be uniformly dispersed throughout the material and in sufficient concentration to give rise to a high scattering density. To remain effective as such a scatterer, its voids must remain constant in number and dimension. Hence, the foam structure must not only be photochemically stable but also mechanically stable.

To obtain a coating whose mechanical characteristics are as stated, it is necessary to select a matrix, blow voids into

it, rigidize it so that the voids are firmly contained, and construct it thick enough to attenuate at least 99% of solar radiation. An attempt to accomplish these aims starts with the unreacted polymer by adding various foaming (or blowing) agents to the polymer and a curing agent/catalyst. The mixture of these, in theory, produces a polymerizing system whose products are gaseous or promote gas generation in the blowing agent. The polymer increases its molecular weight by chain addition, cross-linking, etc., and thus gains physical strength. At a given point, the blowing action is optimum in terms of producing bubbles. These bubbles are dimensionally stable only if the polymer is highly cured and the cure is nearly complete when the gas-blowing action peaks. The correct ranges of physical strengths, viscosities, gas volume generation rates, and temperatures and concentrations of reactants is demanded to achieve the type of coating desired.

The following paragraphs therefore describe continued experiments on foaming of silicones; a discussion of the relevant patent literature examined to date is also presented. Finally, a comprehensive analysis of the photolysis problem as it pertains to microporous coatings is given.

B. Foaming Experiments

1. LTV-602 Emulsions

The use of emulsion techniques was reported in the last triannual report. The slow addition of water makes an

increasingly thick paste with the silicone resin. After a certain point the paste begins to thin out with the continued addition of water. If the addition of water is stopped at a point when the paste is thickest, a film can be obtained that appears to have a very fine particle size. Such emulsions were prepared with the aid of soaps formed from moropholine and oleic acid and from triethanolamine and stearic acid. Hardening of these emulsified compositions required several days; in general, they exhibited a coarse structure. Heating these emulsions at 170°F produced discoloration. This discoloration prompted studies with other emulsifiers. Samples prepared with the aid of Tween 40 (an emulsifier) are listed below:

    Sample 503-3   LTV-602 silicone polymer   30 g
                   SRC-05, catalyst   12 drops
                   Tween 40, emulsifier   2 drops
                   Water   8 g

    Sample 504-1   LTV-602 silicone polymer   30 g
                   SRC-05, catalyst   12 drops
                   Tween 40, emulsifier   4 drops
                   Water   15.2 g

Sample 503-3 solidified to a grey-white color, and sample 504-1 produced a much whiter product. After several days the surface of these samples had indications of losing whiteness. Corrosion of the aluminum-foil pan was also noted. The corrosion was probably due to excess SRC-05 catalyst, which is a strong alkali. Other samples were prepared with smaller amounts of Tween 40 and SRC-05. The evidence of corrosion was

not observed with decreased catalyst addition; however, the
slow loss of whiteness was still observed. Samples prepared
without an emulsifier also lost whiteness after curing to a
white solid.

Two samples were prepared as listed below.

<div align="center">

Sample 508-1

LTV-602	21 g
SRC-05	3 drops
Water	7.5 g

Sample 508-2

LTV-602	21 g
SRC-05	6 drops
Water	7.5 g

</div>

In the second sample the catalyst concentration was increased
to determine whether it would slow the loss of whiteness. It
was thought that a harder polymer, more capable of containing
a bubble, might result if the catalyst was increased. The
faster gellation of sample 508-2 caused air bubbles to be
trapped in the surface layer. These samples were very white;
however, after several days they definitely lost surface
whiteness. This loss, or increase in transparency, first occurs
at the exposed top surface of the specimens and progresses with
time to the unexposed bottom surfaces. The diffusion of mois-
ture out of the cured resin and the subsequent collapse of
the volume occupied by the moisture indicates the need for a

a more rigid resin (a more highly cross-linked resin system
should maintain the very small size bubble without collapsing).
After 7 weeks both samples were clear, apparently indicating
that all moisture had diffused away. It should be noted that
the air bubbles trapped in the surface layers of sample 508-2
are still present. This observation indicates that the moisture
may prevent maximum curing of the sample. Emulsions catalyzed
with tin octoate caused faster curing of the resin but did not
preclude the loss of whiteness from the sample. In fact, the
use of tin octoate as a catalyst caused a greying of the initial-
ly white specimen.

2. Leaching Fillers out of LTV-602

A commercial stripping compound, Diverstrip D-90, was
obtained from the Diversey Corporation to aid in opening the
silicone LTV-602 surface to facilitate leaching out the zinc
oxide pigment. A zinc oxide-pigmented LTV-602 paint that was
placed in Diverstrip D-90 expanded in a short time in a manner
similar to its behavior in benzene and toluene. After a 2-hr
immersion, the sample was removed; it had become stained by
the solution, and only a small percentage of the stain could
be removed by washing with distilled water. No further work
is contemplated with this stripping compound.

3. Foaming of LTV-602

In the preparation of urethane foams, the chemist is aware of the equivalent weights of the polyol, water, and isocyanate and can easily formulate a foaming composition. In any foaming composition, the polymer being formed must be sufficiently strong at the period of peak gas output to contain the small bubble. In other words, the reactions must be in phase, or the gassing reaction will be completed before the polymer structure is formed.

General Electric's LTV-602 silicone polymer is a linear polydimethylsiloxane with a methyl-to-silicon atom ratio of 2.0. It is thought that no side-chains, or branching, is present and that the concentration of SiH is very small, if it is present at all. The absence of SiH is not surprising in light of the lack of reaction and foam generation by the addition of tin octoate. The additiin of tin octoate to a mixture of LTV-602 and blowing agent designated RTV-921 does not produce a foam structure (although bubbles form initially). This is an example of the out-of-phase bubble and polymer formation.

Small amounts (2.5 g) of RTV-921 blowing agent were individually mixed with 2 drops of SRC-05, Nuocure 28, and Thermolite 12 curing agents. Nuocure 28 caused solidification

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of the RTV-921 in approximately 3 min. Bubbles were initially
formed (they could have been due to mixing in air); however,
only a few were contained in the gelled sample. Thermolite
12 caused gellation within a 1-hr period; however, no bubbles
were formed by this catalyst. General Electric SRC-05 caused
gellation within a 24-hr. period with no indication of bubble
formation. Nuocure 28 and Thermolite 12 curing agents caused
noticeable shrinkage in the cured RTV-921.

Two drops of Nuocure 28 (tin octoate) were added to 10 g
of RTV-921 blowing agent and were mixed. The material began
reacting immediately and a foam was formed within a 4 min
period. A higher concentration of catalyst did not produce a
foam. After a 24-hr period, shrinkage was noted. Also,
a slight greying appearance was noted in the foamed structure.

In additional tests, 10 g of LTV-602 were mixed with 2.5 g
of RTV-921. Two drops of SRC-05 and Nuocure 28 were added in
separate experiments. The Nuocure 28-catalyzed system cured
to a firm gel in 45 min. and the SRC-05-catalyzed system
cured to a gel in 1-hr. Foaming did not occur; but a few
large bubbles appeared during the curing period. Foam was
generated in systems in which the Nuocure 28 was added to the
LTV-602 before the addition of the RTV-921 blowing agent.
When the period of time before addition of the RTV-921 was
45 min, no foam was generated. When heated for 5 min, at

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200°F before addition of RTV-921 blowing agent, a foam was generated. In this case the two reactions can be said to be in phase. That is, the foaming occurs at a time when the resin-polymerization reaction has progressed to the point where the polymer being formed is sufficiently strong to contain the gas bubble. The foamed products are generally classed as white when initially produced, but they take on a grey-white appearance within a few days.

4. Use of Metal and Thermit Catalyst T-9

Metal and Thermit Corporation supplies a series of tin catalysts for use in urethane foams and in silicone-curing systems. Catalyst T-9 is a stannous-type catalyst that can be used to replace stannous octoate in most applications where it is specified.

A 10-g sample of LTV-602 was catalyzed with 2 drops of catalyst T-9. This sample cured to a clear, transparent gel in approximately 6 hr. After three weeks there was no evidence of discoloration as in samples prepared with Nuocure 28 (tin octoate).

A 10-g sample of RTV-921 was catalyzed with 2 drops of catalyst T-9. Bubbles were formed on mixing, but they rose to the surface and coalesced. An additional 2 drops of T-9 was added, and mixing produced additional bubbles that were immediately lost at the surface. Within a few minutes the sample started to gel and no bubbles were evident. On

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mixing more bubbles were generated, and air was whipped into the sample. The sample set and then proceeded to crack and split in several places. The experiment was repeated again with only 2 drops of catalyst T-9. When the sample began to set, mixing was started again. More bubbles were generated and the results were the same. A third sample was prepared with 10 g of LTV-602 and 2 drops of T-9. The same initial observations were made; however additional mixing was not performed. The sample set with many large bubbles. Within a 24-hr period considerable shrinkage was noted.

In an attempt to generate foam the following sample was prepared

LTV-602	3 g
RTV-921	1 g
Catalyst T-9	2 drops

These materials were mixed for approximately 45 sec. Within 3 min a foam was formed, but it was of poor quality. This sample had two layers; from the top down approximately 2/3 was foamed, and the remaining 1/3 was clear resin.

A sample was prepared with 5 g of ethyl silicate and 1 drop of T-9. The sample cured to a hard and brittle solid. It should be noted that all samples containing RTV-921 have taken on a greyish appearance, and samples prepared with LTV-602 and with ethyl silicate remain clear when catalyzed with T-9. It is possible that the particular molecular composition

of RTV-921 is responsible for the discoloration. Initially, all foamed samples had a glossy, white appearance.

Further experimentation with ethyl silicate, LTV-602, and various catalysts will be contemplated when the available literature on curing mechanisms has been thoroughly explored. Preparation of our own siloxane materials will be an advantage in future foaming studies.

5. Foaming RTV-60 and Dow Corning RTV-S-5370

General Electric's RTV-60 was foamed with the aid of RTV-921. A catalyst solution was prepared from 11 g of RTV-911, a diluent, and 1 g of Nuocure 28 (tin octoate). The following formulation was prepared

RTV-60	20 g
RTV-921	4 g
Catalyst solution	2.4 g

The catalyst - diluent mixture was added after thoroughly mixing the RTV-921 and RTV-60. A foamed structure was generated in 2 min. The foam was of high density (about 44 #/cu ft according to the literature), and since it is also red in color, it cannot be used as a reflecting coating. A sample of the base material, before the addition of the red iron oxide pigment, has been ordered from General Electric. It is expected that the foam density can be lowered by the addition of a larger percentage of RTV-921 blowing agent.

Dow Corning RTV-S-5370 is a two-component system; the base resin and blowing agent is one component, and the catalyst-diluent is the second component. Six parts of catalyst were added to 100 parts of the base material and mixed for 30 sec. The mixture was poured into an aluminum pan, and the foaming was completed in about 3 min. A soft foam of about 10 lb/ft^3 density, with both large (1/16 in.) and small bubbles, was obtained. Due to pigmentation, the foam is light tan in color. Dow Corning has said that they could not supply the material without this pigmentation.

6. Foaming Q92-009

Dow Corning Q92-009, requiring no catalyst addition, is a dispersion of a room-temperature curing silicone rubber. As the solvent (naphtha) leaves, the dispersion reacts with moisture in the air and cures to a silicone rubber. Twenty-gram samples of Q92-009 were mixed with 3, 6, and 8 g of water. Curing of these samples was much faster than the control sample to which no water was added. The control sample cured to a tough elastomer, but due to the presence of a filler, thought to be silica, the elastomer was somewhat cloudy. The samples prepared by adding water cured to an off-white foam structure; the sample containing the largest amount of water was the whitest of those prepared -- the more water added, the more

foam produced and the smaller the average void size.

When considering the appearance of the control sample, the samples prepared with water added do not appear to have lost any whiteness over a period of 2 months; this contrasts with the behavior of water emulsions of LTV-602, which change from white to transparent during the same time interval. With the filler removed, these samples may offer increased reflectance.

Dow Corning has stated that they will not supply this material in any other form. We have unsuccessfully attempted to have zinc oxide added to the base Q92-009 instead of to the presently used filler.

7. Blowing Agent Thermal Tests

Foamed samples were prepared by using Celogen AZ, Celogen OT, and Unicel NDX blowing agents. The sample prepared from Celogen AZ was yellow in color, although only 1% blowing agent was used. On heating, the color changed to a slightly transparent, light tan color. Heating the sample with Celogen OT to 450°F produced a brown-black color in the sample. The sample prepared with Unicel NDX blowing agent at 400°F produced small yellowish areas on heating. This blowing agent tended to settle to the bottom of the sample.

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Various blowing agents were placed on a hot plate at 600°F; the results are listed in Table 1. On the basis of this test Porophor N should be an excellent blowing agent. Previous studies, however, have indicated that LTV-602 foamed with this material is more degradable than a clear LTV-602 film under ultraviolet exposure in vacuum. These studies are reported in the next paragraph.

8. Effect of UV-Vacuum on Foamed LTV-602

Porofor N blowing agent, in concentrations of 1, 2, 3, 5 and 10%, was mixed with 10 g samples of SRC-05-catalyzed (2 drops/10 g) LTV-602 silicone polymer. Each of the compositions was poured into two aluminum-foil pans and allowed to cure at room temperature. After curing, one pan of each composition was heated at 180°F for 1 hr to facilitate expansion of the blowing agent.

A blown and an unblown LTV-602 specimen, each containing 10% Porofor N, were subjected to ultraviolet radiation in vacuum in Test V-53. The reflectance both before and after only 170 ESH exposure is presented for the unblown and blown (foamed) LTV-602 samples in Figures 1 and 2, respectively. Examination of Figure 1 indicates that the ultraviolet (and visible and infrared) radiation caused the unblown specimen to expand in situ. Even though foaming occurred during the irradiation, considerable damage to the film resulted, as

Table 1

RESULTS OF HEATING VARIOUS BLOWING AGENTS TO 600°F

| Material	Color	Results
Unicel NDX	Light yellow	Bubbled; dark smoke; left brown-black residue, which eventually burned off hotplate.
Unicel ND	Off-white	White-to-tan residue.
Nitrosan	Yellow	Flashed off; left a brown residue, which turned white with continued heating.
Celogen AZ	Yellow	Flashed off; left a white residue, which eventually disappeared.
Celogen OT	White	Left a brown-black (puffed-up) residue.
Kempore 125	Yellow	Same as Celogen AZ.
Porophor N	White	Flashed off; no residue.

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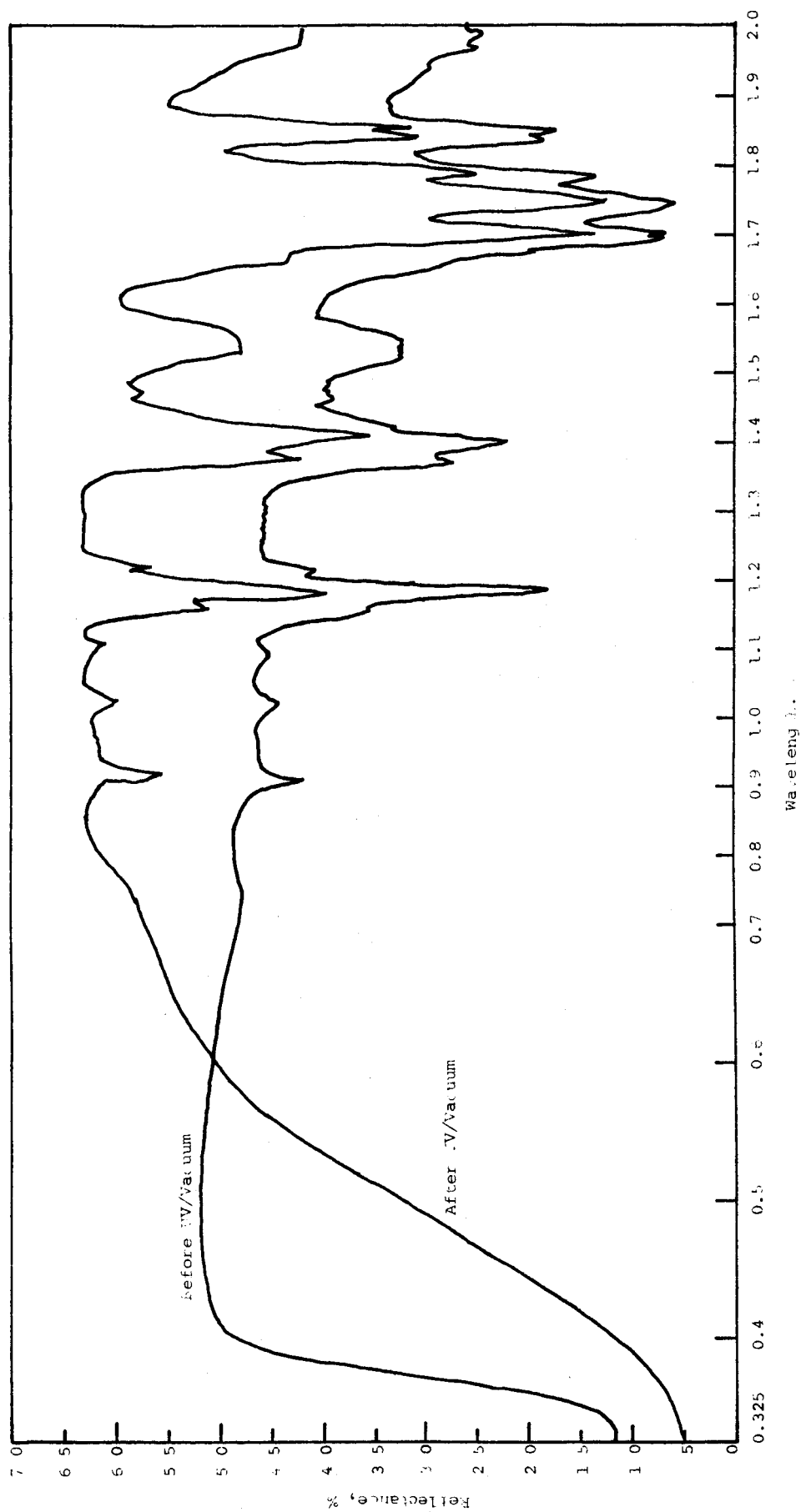
Figure 1

REFLECTANCE OF UNFOAMED LTV-602 FILM
CONTAINING 10% POROFOR N BEFORE AND AFTER ULTRAVIOLET EXPOSURE
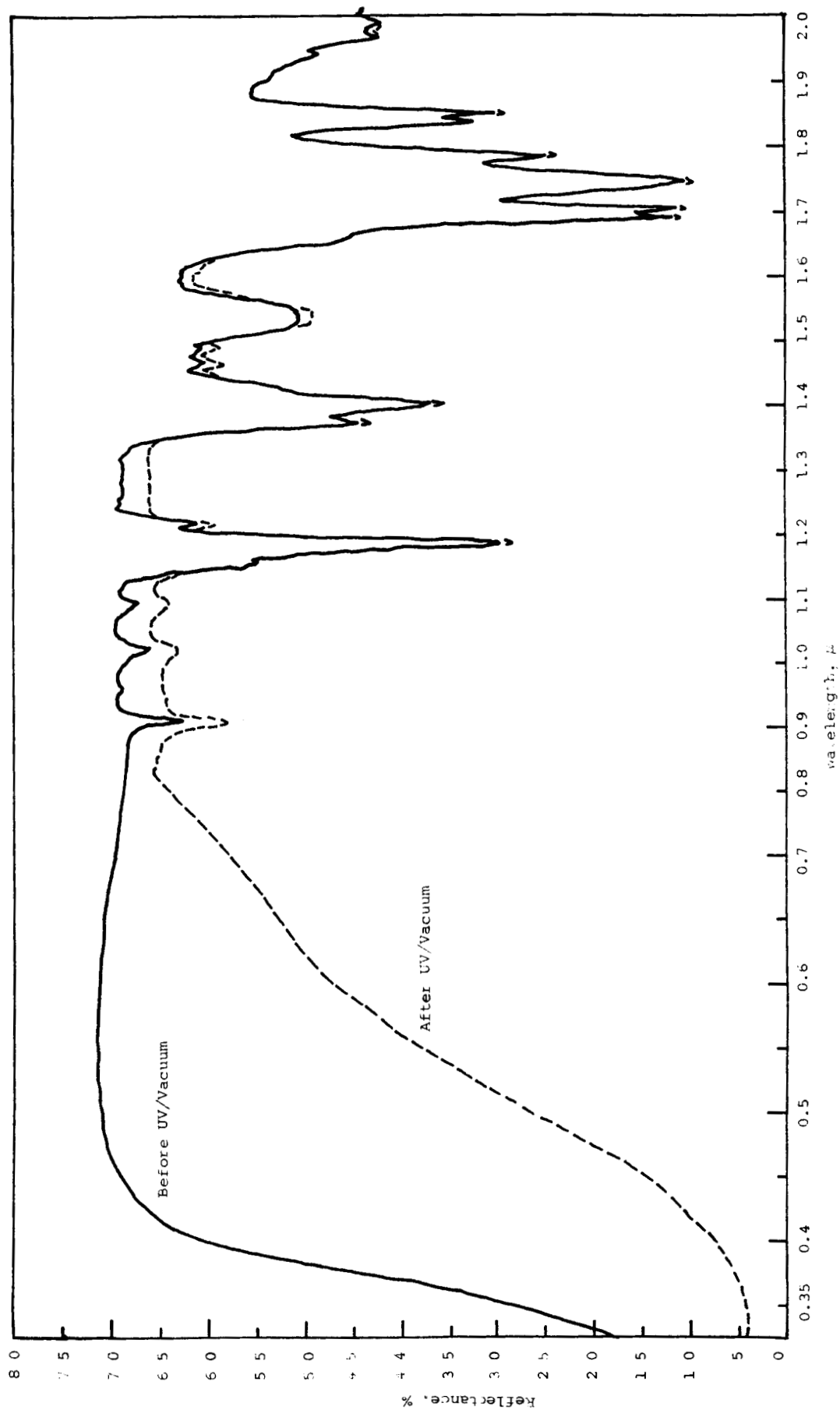
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Figure 2

REFLECTANCE OF FOAMED LTV-602 FILM
CONTAINING 10% POROFOR N BEFORE AND AFTER ULTRAVIOLET EXPOSURE

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evidenced by the severe loss in reflectance in the visible region of the spectrum. Figure 2 shows the effect of irradiation on the optical absorption of the prefoamed LTV-602 specimen.

The damage to the unfoamed specimen did not appear to be as severe as for the prefoamed silicone, as manifested in the decrease in reflectance in the near ultraviolet and visible portions of the spectrum. Indeed, this is more clearly shown by plotting the increase in spectral absorptance, $\Delta\alpha_\lambda$, versus wavelength for both specimens. These differential spectra are shown in Figure 3.

The greater damage resident in the prefoamed specimen is thought to relate to deep and random scattering of the ultraviolet into the foamed white material, whereas, except for some scattering due to the bubbles formed in situ, the ultraviolet passes more directly through the clear, unfoamed specimen. The effect of photolysis of blowing agent residue is accounted for by the fact that the foamed silicone contained no undecomposed Porofor N, but 100% of the Porofor N was initially present in the unfoamed, clear coating. The data presented in Figures 1 through 3 suggest that the damage is due to a different defect in either case as evidenced by the difference in the positions of peak $\Delta\alpha_\lambda$. In any event we can conclude that the problem of ensuring stability of foamed

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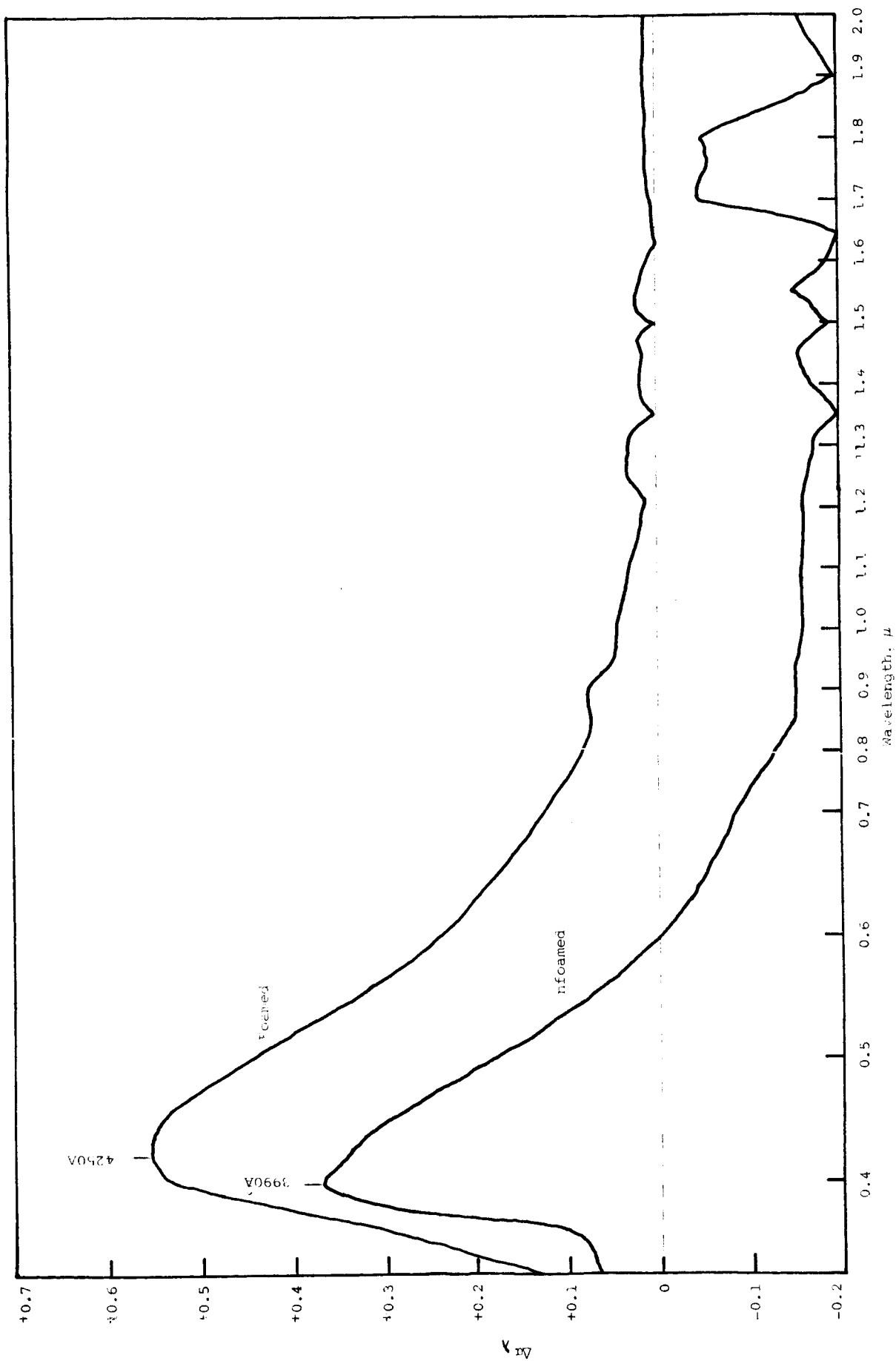
Figure 3

DIFFERENTIAL ABSORPTANCE SPECTRA FOR A FOAMED AND
AN UNFOAMED LTV-602 SILICONE FILM

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systems is of considerable magnitude. An analysis of these

problems is given in a later section.

C. Patent Literature

The patent literature was surveyed for curing mechanisms,

foaming compositions, and catalysts. Information on foaming

compositions and possible foaming reactions was obtained.

However, very little information on the mechanism by which

the various catalysts cause curing of silicone polymers

was obtained. A possible explanation of the influence of

several cross-linking agents is given in US Patent 3,070,566.

A review of the more important patents examined is contained

in the Appendix.

A review of the pertinent literature, in addition to the

patents mentioned above, reveals the paucity of information

about the curing of silicone materials. In general, curing

agents can be divided into the catalytic type and the cross-

linking type. Weak acids, such as acetic, chloroplatinic,

boric, and oleic, and weak bases, such as ammonia, dibutylamine,

triethanolamine, and diethylenetriamine, act exclusively as

hydroxyl-condensation catalysts. On the other hand, strong

acids and bases not only affect hydroxyl-condensation reactions

but promote Si-O-Si skeletal rearrangements. The metal soap

catalysts, such as zirconium acetyl acetonate, tin octoate,

dibutyl tin dimaleinate, and cobalt naphthanate, react with

the carbon-carbon double bonds in drying oils by fairly well-

understood mechanisms. Their action in the curing of silicone compositions is not understood, and although they are considered condensation promoters, the extent to which they become part of the polymer skeleton is not known.

Cross-linking agents such as alkyl orthotitanates, organo-hydrogen siloxanes, and alkyl orthosilicates, and polysilicates also react through the uncondensed hydroxyl groups and become a part of the three-dimensional polymer network.

The only known silicone polymerization reaction that results in the in situ and simultaneous formation of foam involves the use of monomer and prepolymer constituents with silane (Si-H) linkages. The reaction with silanols (Si-OH) and compounds such as quaternary ammonium hydroxide and quaternary ammonium alkoxides results in the formation of the Si-0-Si and Si-0-R linkages and the simultaneous evolution of hydrogen, which, under proper reaction conditions, results in the formation of foams. For these foams to be satisfactory, the polymer must (simultaneously with foaming) gel or set so that the foam does not callapse when the evolution of hydrogen has ceased. It has been found that these reactions occur at a sufficiently rapid rate in the presence of specific catalysts.

D. Discussion and Conclusions

As discussed in an earlier section, a coating composed of appropriately sized voids should in theory scatter light

in a manner very similar to pigmented white films. Unfortunately, the very character of microbubble systems that makes them attractive as solar-reflecting coatings also tends to preclude their use in the ultraviolet environment of space. This can be seen by considering the nature of scattering by totally non-absorbing particles.

First, consider the ray behavior and the path length of ultraviolet in a coating pigmented with an ultraviolet-absorbing pigment (e.g., rutile, zinc oxide, and other white semiconductors). This is shown schematically in Figure 4. Such a pigment effectively absorbs all the ultraviolet in the first two or three interactions, thus providing protection to the matrix. Unlike the ultraviolet—absorbing pigment shown in Figure 4, the ultraviolet-transparent microbubbles depicted in Figure 5 deep-scatter the ultraviolet rays by the very mechanism (multiple refraction) that accounts for the reflectance of white paints as well as foams. Thus, when the ultraviolet-absorbing pigment (Figure 4) is replaced by ultraviolet-transparent microbubbles or pigment particles, the ultraviolet path length in the matrix will be many orders of magnitude greater, and the statistical probability of a photon being absorbed to cause a color center is greatly enhanced. In other words, the penetration and random scatter of the ultraviolet photons within the film will greatly increase the pro-

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Light Beam

Matrix Surface

Matrix

Absorptive
Pigments

Substrate
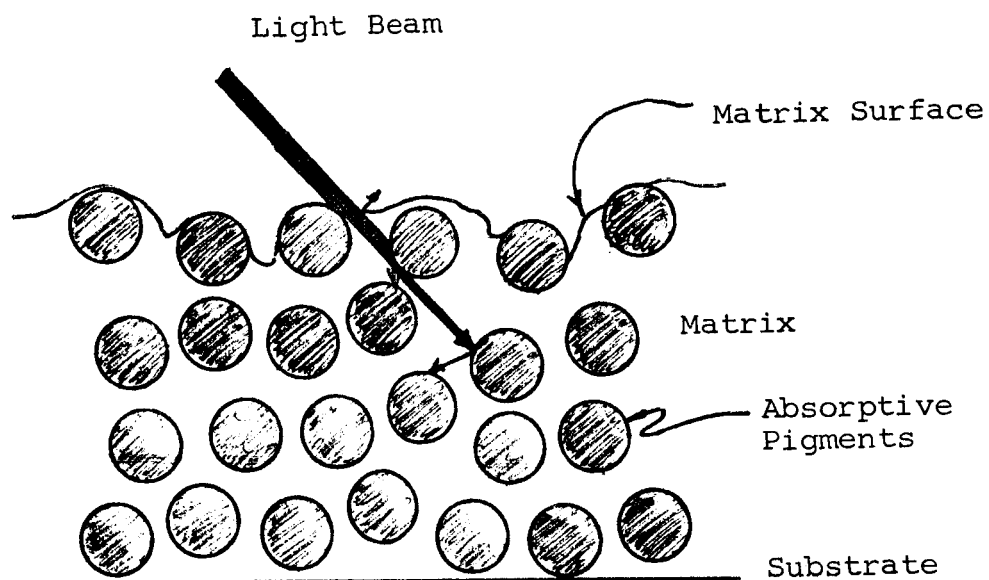
Figure 4

RAY BEHAVIOR IN IDEALIZED PAINT FILM
CONTAINING TOTALLY ABSORBING PIGMENTS

Light Beam

Matrix Surface

Transparent
Pigments

Substrate
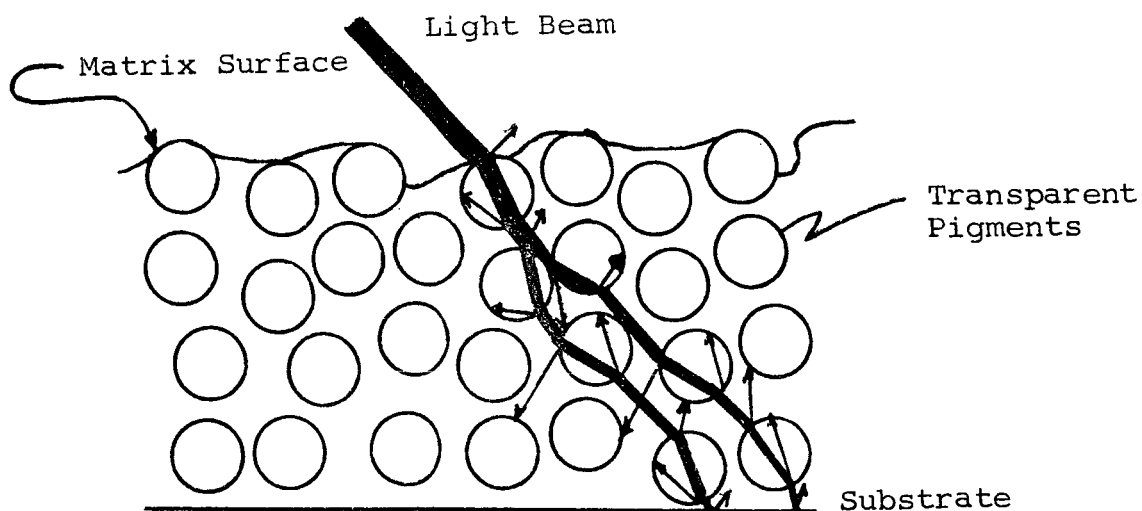
Figure 5

RAY BEHAVIOR IN IDEALIZED PAINT FILM
CONTAINING TOTALLY TRANSPARENT PIGMENTS

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bability of damage, which in this instance, is manifested as increased spectral absorption and evidenced visually by coloration.

From the foregoing discussion and from experimental evidence, the following can be listed as the attributes that are absolutely essential to stable microbubble coatings:

(1) The matrix must be completely transparent to solar radiation - at all wavelengths.

(2) It must have an index of refraction different from unity.

(3) It must have a void structure whose dimensional characteristics are stable and are important in terms of interaction with optical wavelengths.

The key point is that all the components of the matrix must be transparent; otherwise, the absorbing component will eventually color and/or cause other components to degrade. Obviously, if there is no absorption, there will be no damage. Consequently, it is imperative that only pure, highly stable polymers be used as matrices for microporous coatings intended for utilization in the space environment. Commercial foams are not sufficiently stable and in fact have been observed to char after only a few hours of ultraviolet radiation in vacuum. Moreover, micro-bubble coatings based upon the most stable commercial polymers available -- the polydimethylsiloxanes (methyl silicones) -- have been observed to degrade significantly in short space-

simulation tests (see, e.g., the discussion in the preceding paragraphs). In view of the nature of light scattering, this is not surprising, especially considering the influence of polymer contamination on ultraviolet resistance (the chemical foaming and blowing agents leave a residue). A series of tests, which were discussed in the last Triannual Report (IITRI-C6014-13, July 20, 1964), have shown that the toluene solvent (which is ultraviolet-absorbing) <u>remaining after thermal cure (250°F) and after evacuation to 10^{-7} Torr before irradiation</u>, causes significant damage (increase in solar absorptance).

Even though these tests do not permit the conclusion that toluene or other aromatic contaminants are the sole cause of methyl silicone degradation (at least under these circumstances), it is clear enough that these are very strong factors.

Other factors affecting stability include concentrations of aromatic side chains, unreacted catalyst, and various molecular configurations, notably those containing unsaturation (e.g., cross-linked vinyl). Whether stable, low α_s/ϵ microbubble coatings can be prepared depends upon (1) the selection/synthesis of high purity, ultra stable methyl silicone polymers, (2) the rigorour <u>exclusion</u> of contaminants and impurities in the foaming process, and (3) a thorough knowledge of the polymerization chemistry, the curing kinetics, and the gas-

forming chemistry and kinetics. Our previous discussions have indicated the need for a basic study of the last-mentioned item. In order to assure that the gassing reaction is in phase with the polymer forming reaction, we must know its chemistry and kinetics.

III. INORGANIC COATINGS

A. Introduction

As noted at the beginning of this report, the use of thin ultraviolet-reflecting topcoats on zinc oxide systems was partly successful in lowering α_s. The dominance of the unstable second phase, however, was evident in space-simulation experiments. Several non-zinc oxide materials have been examined, and the following effects on optical and stability properties have been observed.

(1) Heat treatment enhances the ultraviolet-vacuum resistance as well as the initial reflectance of pigment powders, particularly in the infrared portion of the spectrum. These increases are due to improved scattering at the longer wavelengths by the increased number of larger particles and to the removal of water, which has strong absorption at 1.9 .

(2) Chemical treatment, such as acid washing, has been found to improve resistance to ultraviolet-vacuum. We strongly suspect that this is due to elimination of impurities.

(3) In addition to zinc oxide, zinc titanate coatings appear relatively stable. An α_s of 0.12 has been achieved with zinc titanate-potassium silicate paints.

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Current inorganic studies can be divided into two general categories: pigment screening and vehicle and coating studies. Pigment screening efforts are generally confined to dielectric pigments, which, unlike semiconductor pigments, do not characteristically absorb near-ultraviolet radiation. The development of low solar absorptance coatings by utilizing semiconductor pigments, such as rutile and zinc oxide, is hampered by the characteristic ultraviolet absorption of such materials -- amounting to as much as 9 to 10% of the sun's energy for zinc oxide and rutile. The criterion, however, as to whether a semiconductor pigment will be examined depends on the degree of absorption it exhibits in the near ultraviolet region. For example, zinc titanate, a semiconductor, exhibits absorption in the ultraviolet, but because it still possesses high reflectance above 0.325μ (37%), it is being evaluated for use in low α_s coatings. Zinc titanate absorbs less than half the solar ultraviolet that is absorbed by zinc oxide.

B. Pigments

During this report period several pigment materials were examined optically and subjected to an ultraviolet-vacuum environment. Included in these studies were four zinc titanate samples supplied by the New Jersey Zinc Company. Sample A-54-2 contains both unreacted zinc oxide and titania; 602-26-1M

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contains no excesses; 602-26-2M contains 50% excess zinc
oxide and 602-26-3M contains 10% excess zinc oxide. The re-
flectances of these materials are presented in Table 2.

Sample A-54-2 is the most reflective, both in the ultra-
violet and infrared. A loss in reflectance is evidenced for
the excess zinc oxide-containing 606-26 series. All samples
exhibited a plateau in the ultraviolet absorbing portion of
the curve at about 0.350 to 0.375 μ. Figure 6 illustrates
these plateaus as well as the compositional effects on their
levels.

Also examined were two materials, beryllia and thoria,
which present health hazards. The use of sintered blocks
facilitated handling and minimized any radioactive and toxic
effects. Solar absorptances, α, for these oxides are as
follows

Material	Solar Absorptance		
----------	α_1	α_2	α
Beryllia	.056	.060	.115
Thoria	.119	.064	.132

The rather high value for the thoria block was due to some
yellowing introduced during sintering, possibly from iron
impurities in fabricating the piece. Limited ultraviolet
absorption was exhibited by both materials; reflectances at
0.325μ were 65 and 44% for beryllia and thoria, respectively.

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Table 2

REFLECTANCES OF ZINC TITANATE MATERIALS

Wavelength, μ	Reflectance, %*			
	Sample			
	A-54-2	60 2-26-1M	602-26-2M	602-26-3M
0.325	36.5	35.5	26.0	25.0
0.375	71.0	57.5	38.0	34.0
0.450	94.0	94.0	92.5	91.0
0.600	95.0	94.5	95.0	93.0
0.700	94.5	93.5	94.0	92.0
1.0	92.5	91.5	91.5	89.0
1.2	93.0	92.0	92.0	88.5
1.4	93.0	92.0	92.0	88.0
1.6	93.0	92.0	91.5	87.0
1.8	92.5	91.0	91.0	84.0
2.0	92.5	90.0	90.0	81.5

*Versus magnesium oxide.

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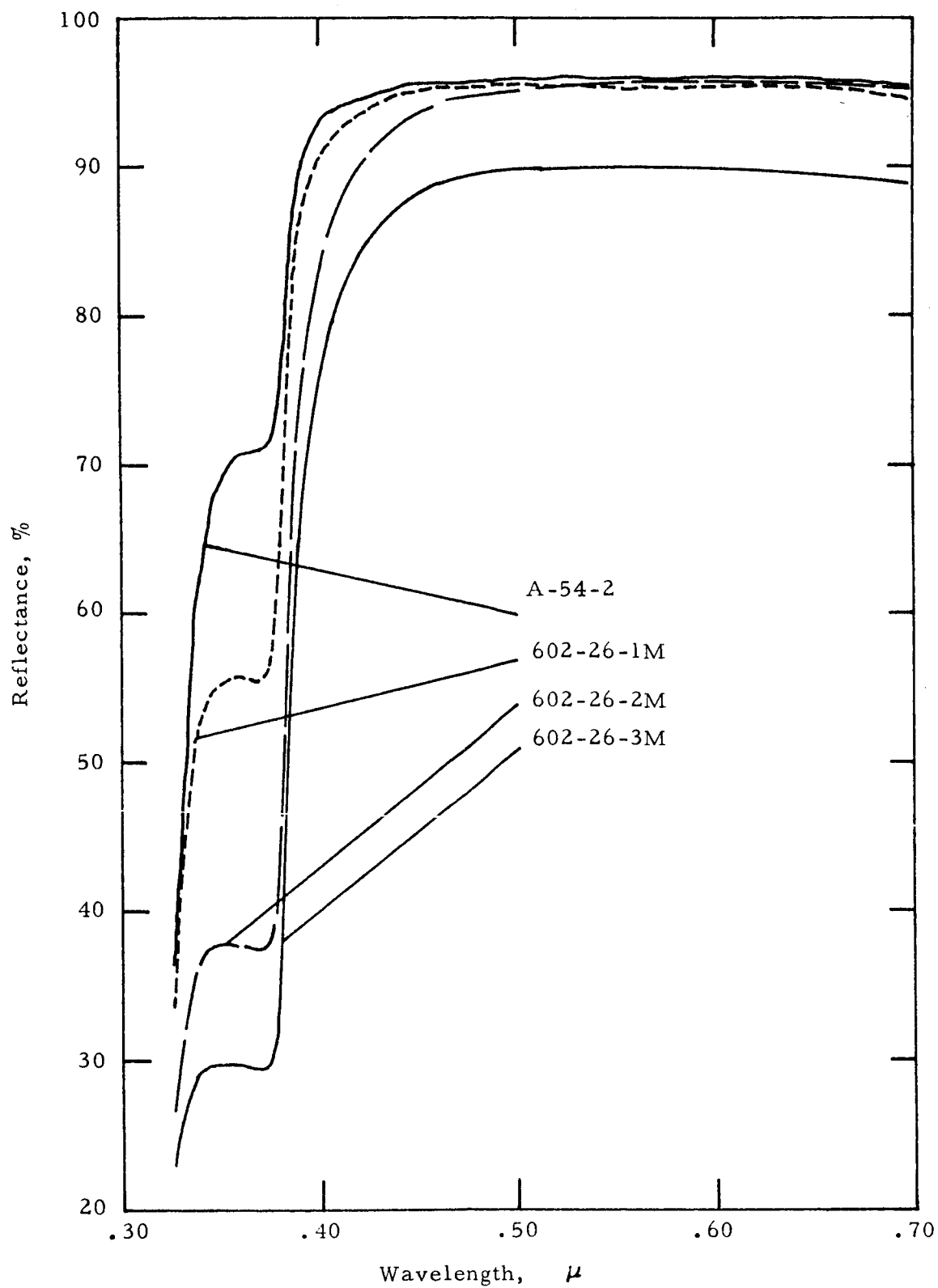
Figure 6

REFLECTANCE OF ZINC TITANATE
IN NEAR ULTRAVIOLET AND VISIBLE REGIONS

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The absence of any unusually promising reflectance coupled with the difficulty in handling precluded further study.

Two space-simulation experiments were conducted to determine the stability of some pigments. The parameters for these experiments were as follows

Test No.	V-55	V-58
Equivalent sun hours (ESH)	690	230
Average solar factor (suns)	9.4	8.5
Pressure level	$<10^{-6}$ torr	$<10^{-6}$ torr

A description of the materials studied is detailed in Table 3. All samples were compacted within copper rings, leaving an exposed face for optical measurements and for exposure to ultraviolet-vacuum. Results for these experiments are tabulated in Table 4.

A decrease in solar absorptance for the china clay was realized both from acid leaching and calcination. The higher reflectance resulted in the infrared portion of the spectrum, as indicated by the α_2 values. Increased stability also occurred as a result of the treatments; the most significant was that from acid leaching.

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Table 3

PIGMENT SAMPLES FOR ULTRAVIOLET–VACUUM STUDIES
(Tests V–55 and V–58)

Test	Sample	Description
V–55	7000	Molochite No. 6, a calcined china clay consisting mainly of mullite with some amorphous silica.
	7001	Molochite No. 6, leached in hot, hydrochloric acid and washed.
	7002	Molochite No. 6, calcined at 800°C for 6 hr and permitted to cool slowly in the furnace.
	7003	Molochite No. 6, calcined at 800°C for 14 hr and quenched by removing to room temperature.
V–58	7030	SP 500 zinc oxide, 700°C/16 hr.
	7031	Dysprosium oxide.
	7032	Lithafrax (lithium aluminum silicate), 800°C/6 hr.
	7033	Zirconia.
	7035	White Barytes (barium sulfate), 800°C/16 hr.
	7036	"Zirconium Spinel" (TAM) 1000°C/16 hr.

Table 4

EFFECT OF ULTRAVIOLET IRRADIATION IN VACUUM
ON OPTICAL PROPERTIES OF PIGMENTS
(Tests V-55 and V-58)

Test	Sample	Exposure ESH	Solar Absorptance			
			$\alpha 1$	$\alpha 2$	α	$\Delta\alpha$
V-55	7000	0	.101	.099	.200	
		690	.182	.108	.290	.090
	7001	0	.099	.085	.184	
		690	.134	.088	.222	.038
	7002	0	.105	.062	.167	
		690	.146	.066	.212	.045
	7003	0	.109	.062	.171	
		690	.152	.068	.220	.049
V-58	7030	0	.095	.056	.151	
		230	.087	.051	.138	-.013
	7031	0	.062	.145	.206	
		230	.108	.141	.249	.043
	7032	0	.045	.062	.107	
		230	.087	.059	.146	.039
	7033	0	.045	.058	.102	
		230	.108	.061	.169	.067
	7035	0	.067	.063	.130	
		230	.141	.066	.208	.078
	7036	0	.050	.057	.107	
		230	.084	.056	.140	.033

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The different cooling rates after calcination were employed to determine whether heat-induced defects, if any, might be frozen in by a rapid quench. At higher temperatures the higher entropy form, the disordered form, will be favored. However, the data for Samples 7002 and 7003 show no such behavior.

In the shorter experiment, V-58, zinc oxide displayed a decrease in solar absorptance upon exposure to ultraviolet-vacuum. The other materials exhibited coloration to varying degrees. A highly unusual series of absorption peaks was exhibited by dysprosium oxide in the near ultraviolet and the infrared, resulting in a relatively higher α. The infrared spectra and curves in the visible before and after irradiation are presented in Figures 7 and 8. The clear superiority of zinc oxide's resistance to ultraviolet-vacuum was again evidenced in this experiment.

C. Vehicles and Coatings

A number of potassium silicate coatings pigmented with various materials have also been subjected to a ultraviolet-vacuum environment. Several compositions, both air-dried and heat-treated, were irradiated in Test V-55, the parameters of which are described above. Table 5 contains both a description of the samples and their optical behavior.
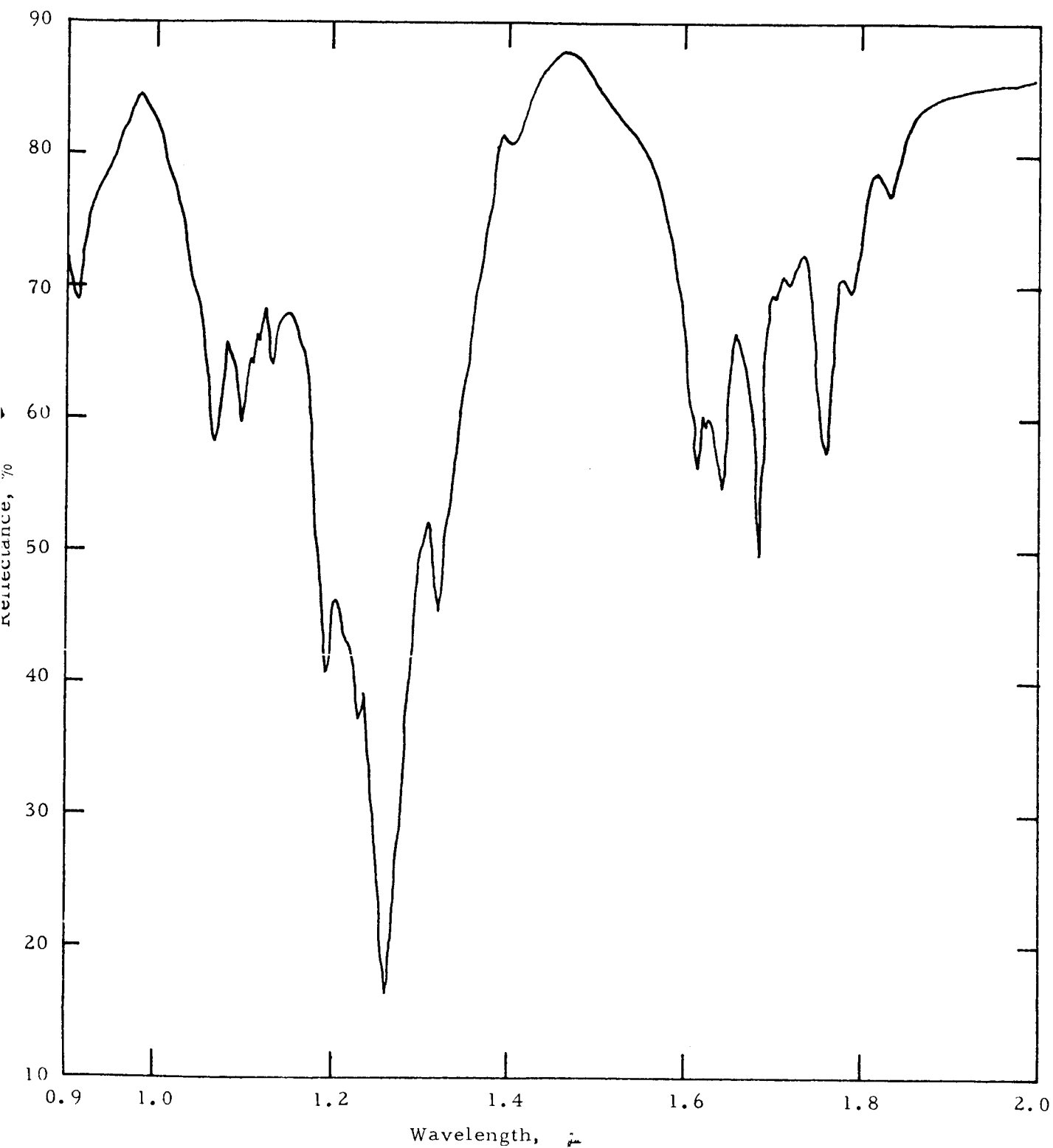
Figure 7
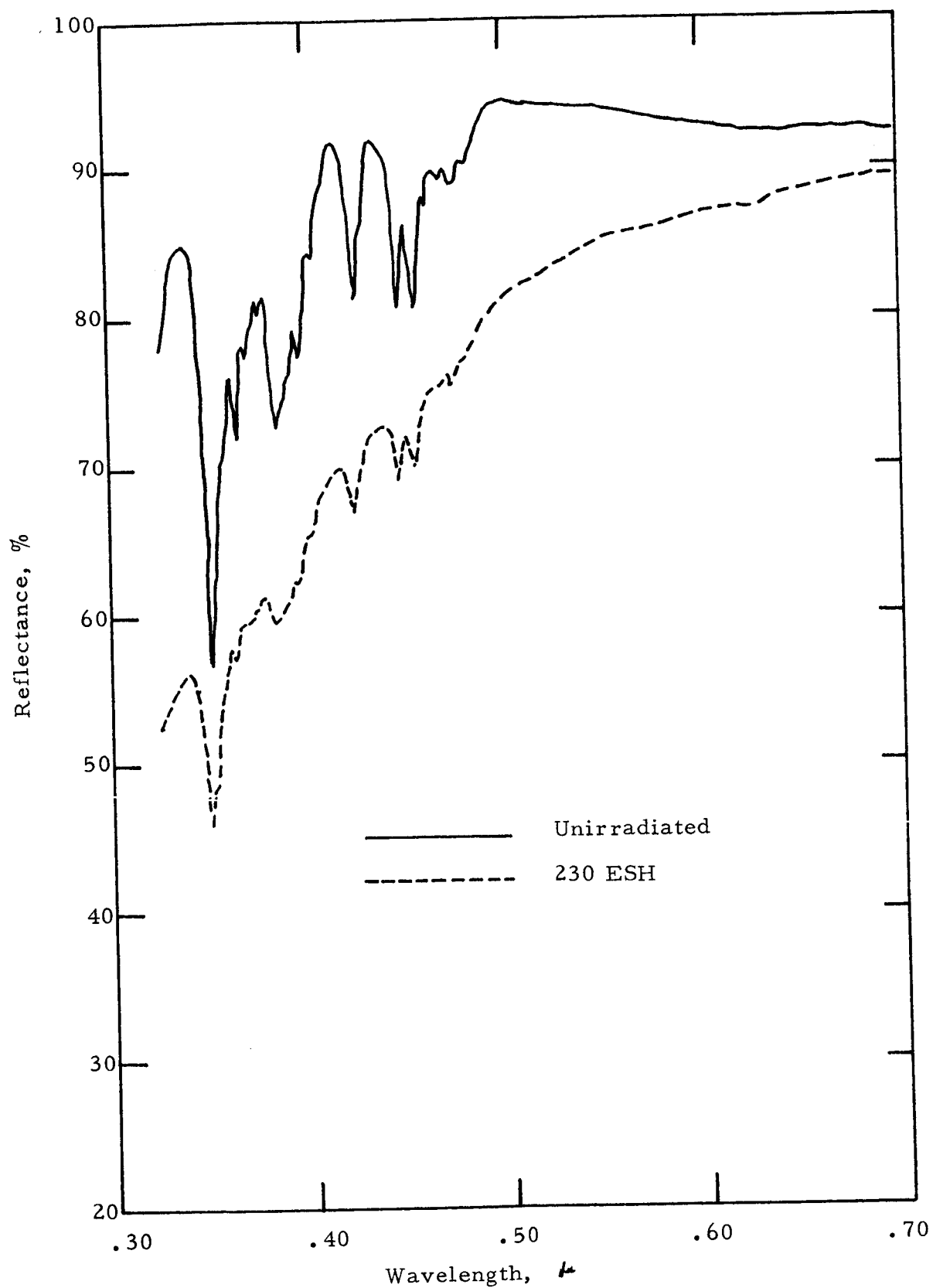
INFRARED REFLECTANCE OF DYSPROSIUM OXIDE

-38-

Figure 8

EFFECT OF ULTRAVIOLET-VACUUM ON NEAR ULTRAVIOLET
AND VISIBLE REFLECTANCE OF DYSPOSIUM OXIDE

-39-

Table 5

EFFECT OF ULTRAVIOLET IRRADIATION IN VACUUM
ON OPTICAL PROPERTIES OF COATINGS
(Test V-55)

Sample No.	Description	Exposure, ESH	Solar Absorptance			
			$\alpha 1$	$\alpha 2$	α	$\Delta\alpha$
7004	Zircon (800°C/16 hr) pigmented silicate. Pigment-to-binder ratio (PBR)=4.30, cured by air-drying.	0	.075	.092	.168	
		690	.149	.091	.240	.072
7005	Same as 7004 plus a 500°C/2 hr heat treatment.	0	.076	.079	.155	
		690	.140	.085	.225	.070
7006	Magnesium aluminate spinel (500°C/16 hr) pigmented potassium silicate. PBR=2.15, cured by air-drying.	0	.038	.099	.137	
		690	.178	.104	.282	.145
7007	Same as 7006 plus a 500°C/2 hr heat treatment.	0	.035	.100	.135	
		690	.185	.116	.300	.165
7008	Zinc titanate-pigmented potassium silicate. The titanate pigment was A-54-2 calcined at 700°C/16 hr. PBR=4.30, cured by air-drying.	0	.059	.063	.122	
		690	.076	.065	.141	.019
7009	Same as 7008 plus a 500°C/2hr heat treatment.	0	.056	.062	.118	
		690	.082	.069	.150	.032
7010	Zirconia-pigmented potassium silicate. PBR=4.30, cured by air-drying.	0	.072	.119	.191	
		690	.105	.118	.222	.031

The spinel coating exhibited a remarkably high reflectance in the visible spectrum, remaining above 90% down to 0.325μ. This is manifested in the low α_1 values for samples 7006 and 7007. However, a relatively high α_2 yielded solar absorptance values well above 0.10. This optical behavior can be partically attributed to the extremely fine particle size of the spinel; however, this very geometry demanded a higher binder content and greater thicknesses for adequate opacity.

Results for the coatings show that only the zinc titanate can be considered as a stable coating. The spinel paints showed disastrous degradation, and the zircon compositions were also significantly discolored. Furthermore, the previously shown beneficial effects of heat treatment on stability did not hold for any of these samples. In fact, the spinel and titanate coatings exhibited the opposite effect.

A coating pigmented with 602-26-1M zinc titanate calcined at 700°C for 4 hr was irradiated in Test V-53 at 170 ESH, 3.5 suns (average), and less than 10^{-5} Torr pressure. The changes for this sample, H-19-53, are detailed below.

Conditions	Solar Absorptance			
	α_1	α_2	α	$\Delta\alpha$
air-dried	.067	.072	.139	
500°C/2 hr	.067	.061	.128	-.011
170 ESH	.092	.067	.159	.031

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On the basis of the experiments to date, A-54-2 zinc titanate appears more stable than the stoichiometric 602-26-1M. The lower solar absorptance obtained with the former also suggests that this material should be emphasized in any future effort involving zinc titanate.

Work was also performed during this period with potassium silicate alone. In an earlier experiment involving this binder applied on aluminum and cured at 150°C to opacity, the results were as follows.

Sample	Exposure, ESH	Solar Absorptance			
		α_1	α_2	α	$\Delta\alpha$
71	0	.101	.203	.304	
	2020	.173	.193	.366	.062
PS7	0	.058	.181	.240	
	2020	.120	.169	.289	.049

The disparity in initial solar absorptance is due to thickness differences. Moderate degradation occurred for both samples ($\Delta\alpha_1$), but a significant improvement was noted in α_2. This corresponds with the α_2 improvement, which almost invariably occurs for pigmented silicate coatings when exposed to ultraviolet-vacuum.

For Test V-57 several vehicle samples, both clear and opaque, were prepared. A thin layer (~ 1 mil) was applied on one group of quartz substrates and a thick film (~ 5 mils) on a second group. Some were merely air-dried, and others

were cured at 110°C. The conditions for this experiment were: 710 ESH, average solar factor of 9.2 suns, and a pressure level of less than 10^{-6} Torr. Reflectance of all films was measured by using the same aluminum backing. A description of the samples and optical data appear in Table 6.

Visual observation after exposure showed that the samples that had seen ultraviolet, including the clear films, had a brownish cast, whereas those wrapped in aluminum showed no coloration. Degradation of thin films, 7022 and 7024, was manifested as a reflectance drop throughout the spectrum examined, 0.325 to 2.0 μ; the ΔR_λ remained quite uniform. These samples as well as 7026 did not reveal the characteristic strong infrared absorption seen heretofore for silicates. In the case of 7023, which opacified during the test, this absorption in the range 1.4 to 2.0 μ was revealed. Furthermore, the visible reflectance improved due to the opacification. Sample 7025 exhibited degradation similar to that for the aforementioned 71 and PS7.

Both the 5-mil samples sheltered from ultraviolet, 7027 and 7029, benefited from the opacification afforded by the vacuum, i.e., the creation of voids to give light scattering. Sample 7028 showed virtually no change.

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Table 6

EFFECT OF ULTRAVIOLET IRRADIATION IN VACUUM
ON POTASSIUM SILICATE FILMS
(Test V-57)

Sample No.	Description	Exposure ESH	Solar Absorptance			
			$\alpha 1$	$\alpha 2$	α	$\Delta\alpha$
7022	One mil, air-dried. Translucent before and after exposure.	0	.319	.248	.567	
		710	.345	.284	.628	.061
7023	Five mils, air-dried. Translucent, opacified during exposure.	0	.321	.293	.613	
		710	.253	.305	.558	-.055
7024	One mil, cured at 110°C. Translucent before and after exposure.	0	.317	.243	.560	
		710	.350	.267	.617	.057
7025	Five mils, cured at 110°C. Opaque before and after exposure.	0	.071	.204	.275	
		710	.123	.203	.326	.051

The following samples were included in the test but were wrapped in aluminum so that they would not see ultraviolet.

7027	Same as 7023	0	.315	.290	.605	
		Vacuum*	.162	.265	.427	-.187
7028	Same as 7024	0	.319	.243	.562	
		Vacuum*	.322	.247	.568	.006
7029	Same as 7025	0	.086	.206	.292	
		Vacuum*	.073	.195	.268	-.024

*Vacuum only.

D. Discussion and Conclusions

We have in reality a dilemma; pigments with low solar absorptance values are in general less stable than those with high values. Although we hope to explore and further elucidate the reason for this dilemma -- whether it is indeed an intrinsic material limitation, or whether the problem has simply not been adequately defined. The guiding idea is to determine whether absorptance increases are directly or indirectly due to ultraviolet irradiation.

In conclusion, it has been shown that:

(1) Heat treatment enhances the initial reflectance of pigment powders and, for most pigments, improves the ultraviolet-vacuum resistance as well. Magnesium aluminate-spinel and zinc titanate-potassium silicate coatings exhibited poorer ultraviolet resistance after heat treatment.

(2) Chemical treatment, such as acid washing, has been found to improve resistance to ultraviolet radiation in vacuum.

(3) Zinc titanate-potassium silicate paints appeared relatively stable in 700 -ESH exposure tests. A solar absorptance of 0.12 has been achieved with a zinc titanate-potassium silicate paint.

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(4)   Severe damage, as manifested in α_s, was exhibited
      by barium sulfate, zirconia, dysprosium oxide,
      lithium aluminum silicate (Lithafrax) and
      zirconium spinel when irradiated as powders for
      230 ESH (listed in decreasing value of $\Delta\alpha_s$).

(5)   Clear silicate films degrade but to a lesser
      extent than opaque potassium silicate films
      (opacified by discontinuities introduced in
      curing the film, resulting in light-scattering
      centers).

IV. METHYL SILICONE PHOTOLYSIS STUDIES

A. Introduction

The ultimate objective of this portion of the program is the synthesis of silicone polymers that are totally resistant to solar radiation. The immediate objectives are (1) to determine the inherent stability of the basic Si-O backbone structure in silicone polymers , (2) to discover (empirically) which sidechain or substituent groups improve stability and which do not, (3) to determine the photomechanics of ultraviolet radiation degradation processes, (4) to assess the influence of contamination on photolysis processes and to identify those contaminants or foreign substances that promote or otherwise affect polymer degradation, and (5) to obtain quantitative information regarding absorptance degradation of polymer materials.

In attempting to keep up-to-date with developments in silicone chemistry, we maintain a constant surveillance of the literature. In so doing, we have scanned a very large number of abstracts, documents, reports, etc., that relate the effects of radiation on silicone materials. By far, the majority of these data pertain to high-energy (gamma) radiation effects. This information is nonetheless useful; many of the reports, etc., deal with the production of color centers and free radicals. The important notion is that the latter are

produced by ultraviolet radiation as well. The literature

gives us many qualitative ideas about what to look for and

what to expect when we expose our materials to ultraviolet

radiation. <u>An important notion is that the properties and</u>

<u>behavior of the color centers are unrelated to the agency</u>

<u>that created them.</u>

B. Polysiloxane Photolysis

The various radiation processes (photolytic, gamma ray,

or electron) cause definite changes in organic materials.

These chemical, and consequently physical, changes that occur

depend on the surrounding environment at any given dose level.

The surrounding environment is considered to be temperature,

type of gas, other reactive species present, pressure, etc.

In polymeric systems the degradative changes generally will

be characterized by gas evolution, color formation, chain

scission, cross-linking (chain scission and recombination),

and various oxidative changes (if oxygen is present). These

degradative processes result from the reactions of various

free radicals and ionic species formed in the polymer as a

result of the radiation processes. The variation in the

type and amount of the particular degradative change will

depend on the immediate environmental conditions.

Almost the entire recorded literature on radiation effects

is concerned with <u>gamma</u>-ray and electron irradiation, especially

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with respect to hydrocarbon polymers. In the work with poly-
siloxanes, numberous discrepancies have been noted. This,
possibly may be due to the type of irradiation as well as to
the total dose. For example, Zack and coworkers[1] have
speculated that phenyl-containing siloxanes are more sensitive
to neutron damage than to _gamma_ rays. Another possible cause
of discrepancy may be the silicone atom itself. Since it
has an additional shell of electrons, its reactions cannot be
related to those of the much more familiar carbon atom.
Silicon is not merely a fat carbon atom and its reactions many
times, are in striking contrast [2] to a hydrocarbon system.
Another discrepancy may be caused by differences in end-blocking
of the polysiloxane. In one case, there may be no endblocking
($-O-Si-OH$); in another there may be variations in the endblocking
(i.e., $-O-Si\equiv R_3$, where R may be all aliphatic or partially
aromatic).

It should be emphasized at this point that, in the litera-
ture surveyed, radiation protection is synonymous with protection
from cross-linking reactions. The optical properties of the

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[1] J. Zack, _et.al._, J. Chem. Eng. Data, _6_, 279 (1961).
[2] H. A. Dewhurst and L. E. St. Pierre, J. Phys. Chem., _64_,
1063 (1960).

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polysiloxanes have been relatively ignored. Thus, we find that although aromatic groups confer radiation protection, only rare mention is made of their color-forming propensities.

In the previous Triannual Report (Report No. IITRI-C6014-13, July 20, 1964) documentation was presented to show that trapped free radicals are directly related to the formation of color centers. In addition, the work of Ormerod and Charlesby [3] was quoted to show that, from their gamma irradiation of unblocked linear polydimethylsiloxane, an ionic cross-linking mechanism took place at -196°C, and stable free radicals could be obtained in vinyl-containing polysiloxanes at room temperature. Thus, a free-radical mechanism appeared to predominate at higher temperatures, and an ionic mechanism predominated at very low temperatures. In a somewhat later paper, Charlesby and Garratt [4] added small amounts of anthracene to the dimethylsiloxane polymer and found no protection against cross-linking. Sulfur gave more protection against cross-linking than could be explained in terms of radical combination -- which is needed to explain the results with anthracene. Benzophenone afforded cross-linking protection, but from the lack

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[3] M. G. Ormerod and A. Charlesby, Polymer, 4, 459 (1963).

[4] A. Charlesby and P. G. Garratt, Proc. Roy Soc. (London), 273A, 117 (1963).

of dose intensity dependence with anthracene combined with the results obtained with the other additives, they concluded, it was necessary to modify some present views on cross-linking. They proposed a different mechanism with each of the additives.

Miller,[5] by using electron radiation, had previously reported that benzene and tetralin both suppressed cross-linking in polydimethylsiloxane oils, with the suppression a function of added aromatic. In a later paper, Miller[6] reported work on trimethylsilyl endblocked polydimethylsiloxane and on diphenylmethylsilyl endblocked polyphenylmethylsiloxane. He concluded that the radiation stability depends not only on total aromatic content but also on the types and positions of the aromatic substitutents. Thus, conjugated aromatic substituents (e.g., biphenylyl and naphthyl) confer a greater stability than a single phenyl group. In addition, the aromatic group is most effective when it is attached to the same Si atom as the radiation-sensitive methyl group; the stabilizing effect of an aromatic group could not be effectively transmitted to a methyl group on a different Si atom.

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[5] A. A. Miller, J. Amer. Chem. Soc. 83, 31 (1961).

[6] A. A. Miller, I. & E.C., Prod. Res. & Dev., 3, 252 (1964).

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However, Koike and Danno [7] by using gamma rays, reported that in polydimethyldiphenylsiloxane the protective effect of the phenyl group may extend over 5 or 6 neighboring units of dimethylsiloxane. Later, Koike [8] independently agreed with the work of Ormerod and Charlesby [3] by concluding that below -100°C the cross-linking of polydimethylsiloxane was due to non-radical processes. In contrast, cross-linking in poly-dimethyldiphenylsiloxane was temperature dependent and due to radical processes. They attempted to relate cross-linking to molecular motion of the group attached to the Si atom. Their polymer was not end-blocked.

C. Synthesis of Linear Polydimethylsiloxane

A linear, low-molecular-weight polymer was prepared by standard techniques but with the scrupulous avoidance of any aromatic contamination.

1. Octamethylcyclotetrasiloxane [9]

A 2-liter 3-neck flask was assembled with a thermometer, stirrer, condenser, and an adding funnel protected with a drying

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[7] M. Koike and A. Danno, J. Phys. Soc. Japan, 15, 1501 (1960)

[8] M. Koike, ibid., 18, 387 (1963).

[9] W. Patrode and D. F. Wilcock, J. Am. Chem. Soc., 63, 358 (1946).

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tube. By using a syringe, the plastic bag technique [10] was
employed for transferring 400 ml of dichlorodimethylsilane
(Union Carbide Corporation) in an atmosphere of prepurified
nitrogen to the adding funnel. The silane was added as
rapidly as dropwise addition would permit to 1200 ml of water,
which had been previously charged into the flask. With the
intermittent application of an ice bath, the temperature was
maintained at 15 to 20°C throughout the vigorously stirred
addition. The nonaqueous phase was extracted with 300 ml of
diethyl ehter, washed with water until neutral, and dried
over sodium sulfate. After filtration, the solvent was re-
moved on a rotating evaporator (Rinco), and the residue ($\sim$ 250 ml)
was distilled rapidly through a 6 x 3/4 in insulated Vigreaux
column. The fraction boiling at 164 to 171°C/745.5 mm was
collected and weighed (123 g).

This fraction was then carefully redistilled by using
the previously described apparatus. The fraction boiling
at 170.0 to 173.0°C/738.7 mm was collected in two equal parts.
Each of the two parts had an index of refraction, $N_D^{27.6}$ =
1.3932. This value is in essential agreement with that

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[10] L. U. Berman, IIT Research Institute, unpublished description.

reported by Hunter [11] and the boiling point reported[8,9] is the same. A total of 81 g of the cyclic tetramer was obtained.

2. Linear Polydimethylsiloxane (by catalytic rearrangement[9])

Into a 250 ml g.s. Pyrex bottle was charged 52 ml of the cyclic tetramer (octamethylcyclotetrasiloxane), 25 ml diethyl ether, and 9.6 ml of conc. sulfuric acid. The stopper was secured by wire and the bottle allowed to shake in a Eberbach shaking machine for 24 hr at ambient room temperature. After this time, the thick mass was diluted with 50 ml of diethyl ether, 25 ml of water was added and the bottle was shaken for 1 hr. The solvent was separated and washed with three 10-ml portions of water. The still-acid solvent layer was diluted a little further with ether and dried over solid, anhydrous potassium carbonate.

The filtrate was placed on a rotating evaporator to remove the solvent, and the residue was distilled through a long Claisen adaptor by using a Woods' metal heating bath. At still-pot temperatures up to 360°C, a few milliliters of liquid distilled at temperatures up to 117°C. The residue was allowed to cool in an atmosphere of prepurified nitrogen.

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[11] M. J. Hunter, et.al., J. Am. Chem. Soc. 68, 667 (1946).

The molecular weight of the residue averaged 3,030 by Mechrolab vapor pressure osmometer determination.

Analysis [12], Found: H, 7.77, 8.09; C, 31,90, 31.84; Si, 34.59, 34.89. Calcd. for $(CH_3)_2SiO$; H, 8.16; C, 32.38; Si 37.86.

The absorption spectrum of this polymer (in isooctane) was better than 98% transparent from 4,000 to less than 1900 A.

The $CH_3:Si$ ratio was close to the theoretical value of 2. At the pressures required for photolysis and at room temperature, about 10 to 15% of the polymer distilled over a 16-hr period.

D. Discussion and Conclusions

As previously noted, chain scission and color formation are interrelated in the sense that the former is one precursor of the latter. Aromatic contamination may act as energy traps and store energy for relatively long periods of time. Through such insidious mechanisms as energy transfer and photosensitization, in which the energy donor is not damaged, infinitesimally small amounts of aromatic contaminants can give rise to inordinately large deleterious effects. However, the exact

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[12] Schwarzkopf Analytical Labs., Woodside, N.Y.

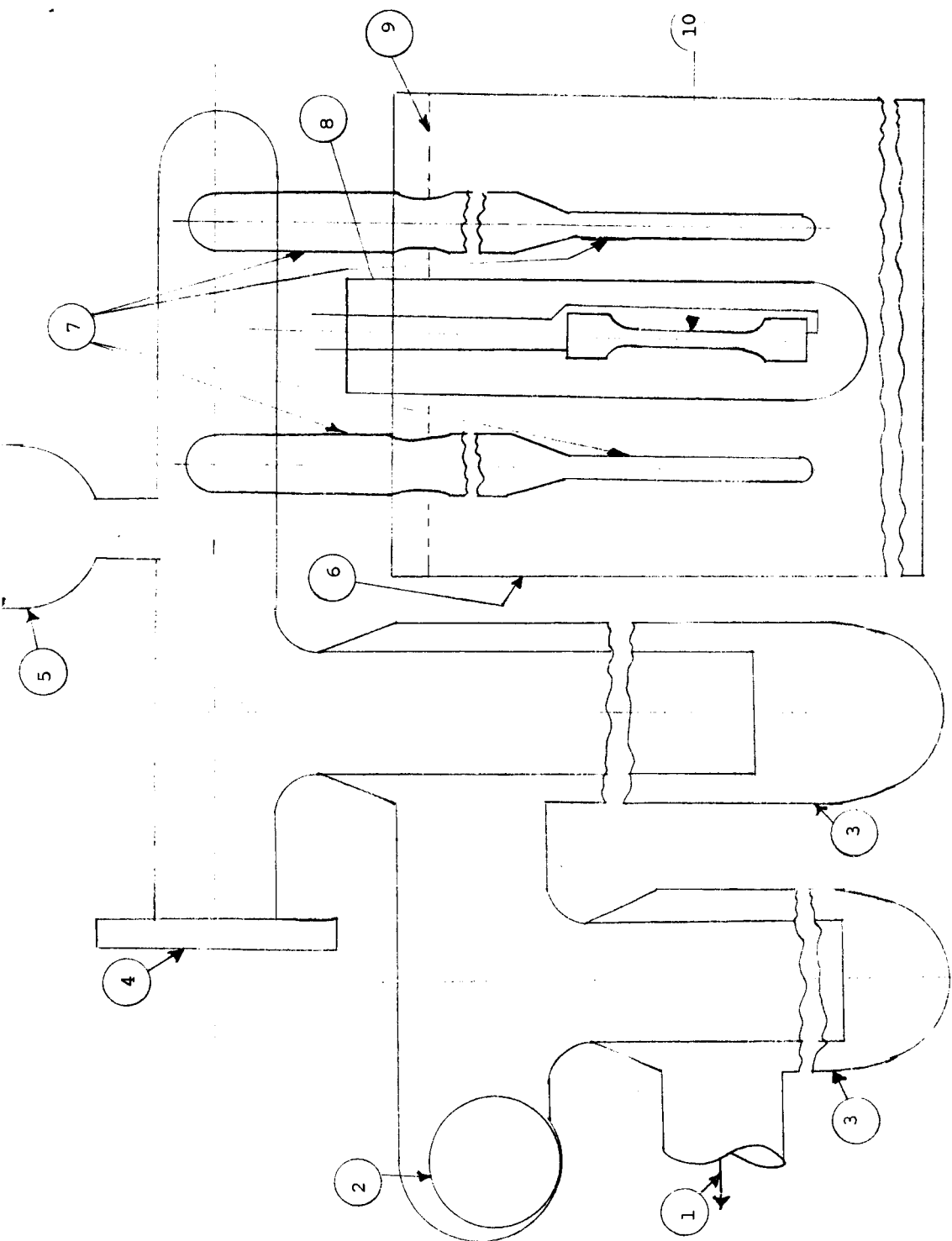effects of very low aromaticity have not been thoroughly investigated.

In the preceding section, the synthesis of a linear polydimethylsiloxane was described. Its absorption spectrum showed it to be more than 98% transparent from 4000 to less than 1900 A. This polymer will be irradiated in the apparatus just completed and presently undergoing check out tests (Figure 9). The ultraviolet-induced photolytic degradation will be initiated in duplicate 3 or 4 mm outer diameter Suprasil quartz tubes. The gases from one will be analyzed by mass spectrometry; the other sample by ESR (electron spin resonance) techniques in attempts to determine the nature and extent of free radical formation.

ESR techniques have been employed for the detection of trapped free radicals in various hydrocarbon polymers.[13] Its application to siloxane polymers is relatively recent,[1,3] and its interpretation depends on several unestablished assumptions. For this reason, the ESR data is not definitive at present, and other comparison data (gas evolution analysis, gelation rate, etc.) are employed in conjunction. In our work, the unirradiated polymer will be used as a reference

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[13] C. K. Jen, "Formation and Trapping of Free Radicals," Bass and Broida, Editors, Chapter 7, Academic Press, New Yor, 1960.

Figure 9

ULTRAVIOLET PHOTOLYSIS APPARATUS

1 – 1" Tube to Mercury Diffusion Pump
2 – Diffusion Pump Isolation Valve, magnetically operated
3 – LN_2 Cold Trap
4 – Gas Analyzer Tube mounting Flange
5 – Bryard – Alpert Pressure gauge
6 – Liquid Nitrogen Dewar
7 – Suprasil Sample tubes and Pyrex pinch off tubes
8 – Lamp Isolation LN_2 Dewar
9 – Liquid N_2 level
10 – AH6 Lamp

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in order to interpret the data obtained.

The solution of the major problems in the successful design of a completely stable polymethylsiloxane must proceed from the synthesis and study of well-characterized polymers to the study of ultraviolet degradation mechanisms – mechanisms that are a function of chemical composition and structure of the polymer, of the nature, type and quantity of contaminant(s), and of such environmental parameters as oxygen pressure, and sample temperature. That each of these factors plays a part in the photolytic degradation mechanisms of silicone polymers has been conclusively established. How important each is remains to be seen.

APPENDIX

PATENT LITERATURE REVIEW

A. General Information

U.S. Patent No. 3,033,807 is concerned with coloring organopolysiloxanes with iodine and various metal octoates and naphthenates. By adding the metallic salt to the organopolysiloxane and iodine, a color was obtained that was different from the magenta caused by the iodine. Subsequent addition of another metal salt to the new colored materials results in another color change. What is important here is that a polysiloxanol resin (furnished by General Electric) contains ethyl silicate to allow low-temperature curing. The resin was not identified. In another example the gum base used by General Electric for its RTV-40, -60, etc., rubber compound was mixed with a small amount of Ethyl Silicate 40, a Carbide and Carbon Chemicals Corporation product, and dibutyl tin dilaurate to facilitate curing. It is not known if ethyl silicate is present in the iron oxide-pigmented commercial RTV-60, but its presence is suspected since the material slowly solidified with time and heat.

The patent further states, for organopolysiloxanes curable at room temperature, an organic silicate cocatalyst is generally used with the metallic salt of a carbolic acid. Polyethyl

silicate, $(C_2H_5O_4)Si$, is the preferred cocatalyst.

U.S. Patent No. 3,070,566 refers to room temperature-vulcanizing elastomers that consist of a mixture of linear diorganosiloxane polymers selected from (1) mixtures of hydroxy end-blocked diorganosiloxane and (2) diorganosiloxane polymers with both triorganosilyl end-blocking and hydroxy end-blocking, cross-linking agent, and catalyst. The catalyst is selected from the group consisting of acetic acid, dibuty-lamine, chloroplatinic acid, lead octoate, zirconium acetyl acetonate, tin oleate, tetraethyl lead, dibutyl tin dilaurate, dibutyl tin dimaleinate, dibuty tin diacetate, tin ricinoleate, cobalt naphthenate, chromium acetyl acetonate, phenyl mercury acetate, triethanolamine, polyethylene-imine, boric acid, and oleic acid. The cross-linking agents can be alkyl orthosilicates, alkyl polysilicates, and organohydrogensiloxanes. For example, ethylorthosilicate, methylorthosilicate, ethyl polysilicate, and propylsilicate are operable cross-linking agents. The triorganosilyl end-blocked polymer is chemically tied into the hydroxy end-blocked polymer by the cross-linking reaction. The Si-O bonds in the siloxane polymers in the mixture are probably split and recondensed under the influence of the cross-linking catalyst. (The patentability is not dependent on this explanation.)

U. S. Patent No. 2,449,572 relates the influence of soluble metal salts of organic acids on the curing of polysiloxane resins. A polysiloxane resin was prepared by hydrolysis and condensation of a mixture of 90% methyl trichlorosilane and 10% dimethyl dichlorosilane. Toluene and butanol solutions of the resin were heated in boiling water under reflux conditions with known amounts of soluble metal naphthenates. Gelling times ranged from 1 min to 18 hr, whereas (with no catalyst) several days heating were required to attain the same degree of cure. U.S. Patent No. 3,033,807 refers to this patent in the discussion of the advantage of a catalyst (ethyl polysilicate) to enable relatively rapid room-temperature curing. This early patent (August 1944) is used as a reference patent on many of the more recently granted patents. The patent further states that the specific effect of the soluble organic acid metal salt on the cure of the polysiloxane resins is not fully understood. Since polysiloxane resins are not known to contain active double bonds or other readily oxidizable groups, the catalytic effect of the metal salt evidently does not involve an oxidation reaction. However, these metal salts are used as driers in drying oil compositions.

U.S. Patent No. 3,032,530 is concerned with the preparation of polysiloxane gums with the aid of specific isocyanates. The author states that the condensation of silicon-

bonded hydroxyls and the rearrangement of Si-O-Si bonds are the
two primary mechanisms by which siloxanes are polymerized in
commercial operation. Weak acids, such as acetic acid, and
weak alkalis, such as ammonia or amines, act exclusively as
hydroxyl-condensation catalysts. Materials such as strong
acids and bases act as both condensation and Si-O-Si bond-
rearrangement catalysts. Again, the actual action of the
catalyst is not explained. In fact, the author states that
the precise mechanism for the reaction is not apparent in
his patent on the action of specific isocyanates. Since the
by-products of this reaction are carbon dioxide and a disub-
stituted urea, he believes that the reaction may occur accord-
ing to the following equations:

$$2 \ \equiv SiOH \ \xrightarrow{\text{RNCO}} \ SiOSi \ + \ H_2O$$

$$H_2O \ + \ 2RNCO \ \longrightarrow \ CO_2 \ + \ (RNH)_2CO$$
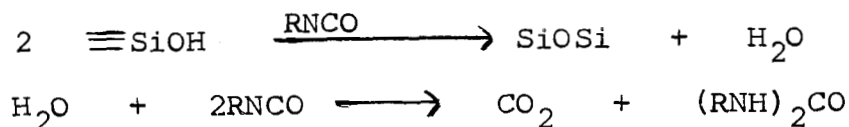
The curing of General Electric's LTV-602 with catalyst
SRC-05 is believed to to be a hydroxy condensation. It is
not known whether the water by-product further reacts or is
lost by diffusion and evaporation. It is also not known
whether the LTV-602, as supplied, has a cocatalyst or cross-
linking agent to facilitate the low-temperature vulcanization.

B. Foaming Compositions

Three patents assigned to Dow Corning Corporation have been obtained and are reviewed in this section. (A British patent assigned to Midland Silicones Limited has been ordered.)

U.S. Patent No. 2,956,032 describes the addition of specific materials to make the resultant foams fire retardant. Without considering the fire retardant additives, the foams are prepared from (1) an organopolysiloxane containing silicon-bonded OH groups with a viscosity of at least 50 cP at 25°C and having per silicon atom on the average from 1.9 to 2 radicals of the group consisting of monovalent hydrocarbon radicals, halogenated monovalent hydrocarbon radicals and hydrogen atoms, (2) up to 50% by weight based on the weight of siloxane (1) of a hydroxylated compound selected from the group consisting of silanols, low molecular weight hydroxylated siloxanes, water, carboxylic acids and alcohols of less than twelve carbon atoms, and (3) a stannous salt of a carboxylic acid in an amount sufficient to give from 0.1 to 10% by weight tin based on the weight of siloxane (1). Catalysts include, for example, stannous acetate, stannous oleate, stannous stearate, stannous linoleate, stannous naphthenates, stannous benzoate, stannous naphthoate, stannous succinate, stannous sebacate, stannous lactate, stannous maleate, stannous crotonate, stannous salicylate, stannous phthalate, stannous mendelate, stannous cinnamate, and the stannous salt of phenyl

acetic acid.

U.S. Patent No. 3,070,555 is essentially the same as No. 2,956,032, except that the fire-retardant aspect of the foam is omitted.

U.S. Patent No. 3,024,210 discusses the preparation of foam by mixing (1) an organopolysiloxane having per silicon atom on the average of from 1 to 1.8 organic radicals of the group consisting of monovalent hydrocarbon radicals, halo-genated monovalent hydrocarbon radicals, and halophenoxymethyl radicals, at least 1 percent by weight of the siloxane units in said polysiloxane having at least 1 hydrogen atom attached to the silicon atom thereof; (2) from 0.001 to 30% by weight based on the weight of said polysiloxane of a catalyst selected from the group of quaternary ammonium hydroxides, quaternary ammonium alkoxides, quaternary ammonium salts of aliphatic carboxylic acids, said acids having at least 5 carbon atoms, and quaterary ammonium salts of silanols; and (3) a non-acidic hydroxylated compound selected from the group consisting of silanols, water, and organic non-acidic alcoholic compounds. Of the catalysts known to cure siloxanes, the ones mentioned in this patent are claimed to be far superior to any others for the preparation of room-temperature foams. Of the catalysts used in the examples, betahydroxyethylbenzyldimethyl-ammonium butoxide (20% in butanol) was the most frequently

mentioned. A fourth and optional ingredient that can be employed in producing the foams of the disclosure is an alkoxy polysilicate. The polysilicate gives improved all structure and faster hardening time at room temperature.

The chemical abstract for British Patent No. 876,619 indicates that a hydroxylated poly(dimethylsiloxane) (1) of 50 to 1000 cs. viscosity, containing 1 to 75% of an SiH unit is mixed with up to 50% of a hydroxylated compound (silanol, glycol) and 0.1 to 10% ten carboxylate (stannous octoate) to form a foam. Compound (1) can be either a copolymer or a mixture of SiOH and SiH polysiloxanes.

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